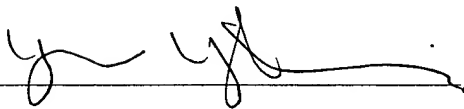


VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome,
Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am
conversant with the Japanese and English languages and that I am the
translator of the documents attached and certify that to the best of
my knowledge and belief the following is a true and correct English
translation of the Japanese Patent Application No. Hei 10-306233
in the name of KANEKA CORPORATION.

Dated this *6th* day of *August*, 2004

A handwritten signature in black ink, appearing to read 'Yasuo Yasutomi', is written over a horizontal line.

Yasuo Yasutomi

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[Title of the Invention] POLYMER

[Scope of Claims for Patent]

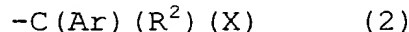
[Claim 1] A multiblock copolymer which is produced by adding
5 a polymer (I) containing an alkenyl group at one terminus and
a group serving as an initiator group for atom transfer radical
polymerization at the other terminus to an atom transfer radical
polymerization system.

[Claim 2] The polymer according to Claim 1, wherein the terminal
10 alkenyl group is represented by the general formula 1:



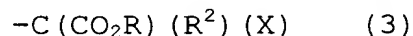
(wherein R^1 represents a hydrogen atom or a hydrocarbon group
containing 1 to 20 carbon atoms).

[Claim 3] The polymer according to Claim 1 or 2, wherein the
15 group serving as an initiator group for atom transfer radical
polymerization of the polymer (I) is represented by the general
formula 2:



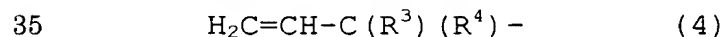
(wherein Ar represents an aryl group which may optionally have
20 a substituent, R^2 represents a hydrogen atom or a hydrocarbon
group containing 1 to 20 carbon atoms, and X represents chlorine,
bromine or iodine).

[Claim 4] The multiblock copolymer according to Claim 1 or 2,
wherein the group serving as an initiator group for atom
25 transfer radical polymerization of the polymer (I) is
represented by the general formula 3:



(wherein Ar represents an aryl group which may optionally have
a substituent, R^2 represents a hydrogen atom or a methyl group,
30 R represents an organic group containing 1 to 20 carbon atoms,
and X represents chlorine, bromine or iodine).

[Claim 5] The multiblock copolymer according to any of Claims
1 to 4, wherein the terminal alkenyl group is represented by
the general formula 4:



(wherein R^3 and R^4 may be the same or different and each represents a hydrogen atom or a monovalent organic group).

[Claim 6] The multiblock copolymer according to any of Claims 1 to 5, wherein, in the general formula 1, R^1 is a hydrogen atom.

5 [Claim 7] The multiblock copolymer according to any of Claims 3 to 6, wherein, in the general formula 2, R^2 is a hydrogen atom.

[Claim 8] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a vinyl polymer.

10 [Claim 9] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a polyolefin polymer.

[Claim 10] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a hydrocarbon polymer.

[Claim 11] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a polyester polymer.

15 [Claim 12] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a polyether polymer.

[Claim 13] The multiblock copolymer according to any of Claims 1 to 7, wherein the polymer (I) is a polysiloxane polymer.

20 [Claim 14] The multiblock copolymer according to any of Claims 1 to 13, wherein the polymer (I) has a glass transition point not lower than 25°C and the polymer chain newly produced by atom transfer radical polymerization with the addition of polymer (I) has a glass transition point not higher than 25°C, or the polymer (I) has a glass transition point not higher than 25°C
25 and the polymer chain newly produced by atom transfer radical polymerization with the addition of polymer (I) has a glass transition point not lower than 25°C.

[Claim 15] The multiblock copolymer according to any of Claims 1 to 14, wherein the polymer (I) has the number average molecular
30 weight of 500 to 100000.

[Claim 16] The multiblock copolymer according to any of Claims 1 to 15, wherein the polymer (I) has the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n) (M_w/M_n) as determined by gel permeation
35 chromatography of less than 1.8.

[Claim 17] The multiblock copolymer according to any of Claims 1 to 16, wherein the polymer (I) is produced by controlled radical polymerization.

5 [Claim 18] The multiblock copolymer according to Claim 17, wherein the polymer (I) comprises a vinyl polymer produced by atom transfer radical polymerization.

[Claim 19] The multiblock copolymer according to Claim 18, wherein the metal complex to serve as a catalyst for atom transfer radical polymerization is selected from the group
10 consisting of a copper, nickel, ruthenium or iron complex.

[Claim 20] The multiblock copolymer according to Claim 19, wherein the metal complex to serve as a catalyst for atom transfer radical polymerization is a copper complex.

[Claim 21] The multiblock copolymer according to Claim 17,
15 wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using a chain transfer agent.

[Claim 22] The multiblock copolymer according to any of Claims 18 to 20, wherein the polymer (I) is produced by using an alkenyl-containing initiator.

20 [Claim 23] The multiblock copolymer according to Claim 22, wherein the polymer (I) is produced by using an allyl halide as an initiator.

[Claim 24] The multiblock copolymer according to any of Claims 18 to 20, wherein the polymer (I) is produced by starting
25 polymerization by a functional group-containing initiator and then converting the functional group introduced into the polymer terminus to the functional group represented by the general formula 1.

[Claim 25] The multiblock copolymer according to Claim 24,
30 wherein the functional group is a hydroxyl group.

[Claim 26] The multiblock copolymer according to Claim 25, which is obtainable by converting the hydroxyl group by a compound containing the group represented by the general formula 1 and an isocyanate group.

35 [Claim 27] The multiblock copolymer according to any of Claims

1 to 26, wherein the polymer chain newly produced by atom transfer radical polymerization with the addition of polymer (I) has a glass transition point not higher than 25°C.

5 [Claim 28] The multiblock copolymer according to any of Claims 1 to 27, wherein the polymer (I) is added to an atom transfer radical polymerization system of a (meth)acrylic monomer.

[Claim 29] The multiblock copolymer according to any of Claims 1 to 28, wherein the atom transfer radical polymerization with the addition of the polymer (I) is started by a di- or more
10 functional initiator.

[Claim 30] The multiblock copolymer according to any of Claims 1 to 29, wherein the polymer (I) is used as an initiator for the atom transfer radical polymerization.

[Claim 31] The multiblock copolymer according to any of Claims
15 1 to 29, wherein the polymer (I) is added in the course of the atom transfer radical polymerization.

[Claim 32] The multiblock copolymer according to any of Claims 1 to 29, wherein the polymer (I) is added after completion of the atom transfer radical polymerization, and a radically
20 polymerizable monomer is added simultaneously or thereafter.

[Claim 33] A thermoplastic elastomer which comprises, as the main component thereof, the multiblock copolymer according to any of Claims 1 to 32.

[Claim 34] An impact resistance improving agent which comprises,
25 as the main component thereof, the multiblock copolymer according to any of Claims 1 to 32.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

30 The present invention relates to a method of producing a multiblock copolymer comprising various polymers and a vinyl polymer, the polymer and its use.

[0002]

[Prior Art]

35 Block copolymers composed of different polymer block

species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block copolymers using them. When radical polymerization is employed, however, it is difficult to control the polymerization, since the growing species radical is unstable. In recent years, examples of the so-called living radical polymerization in which the growing radical in the radical polymerization is inhibited from undergoing coupling have been reported.

[0003]

As examples, there may be mentioned, among others, the method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and "atom transfer radical polymerization" (ATRP) in which an organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. Living radical polymerization hardly undergo termination reaction and give polymers narrow in molecular weight distribution (M_w/M_n being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization regarded as difficult to control because of a high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other, among others.

[0004]

Among such "living radical polymerization methods", in the "atom transfer polymerization methods" for polymerizing vinyl monomers using an organic halide, sulfonyl halide or the like as an initiator and a transition metal complex as a catalyst (for example, in Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614;

Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721), in addition to the characteristic features of the above-mentioned "living radical polymerization methods", halogen, etc., relatively favorable for functional group conversion reactions is contained at its terminus and the degree of freedom is high in designing the initiator or catalyst.

[0005]

When these characteristics of the living radical polymerization are used, it becomes possible to obtain a block copolymer of a vinyl polymer, which has been difficult to be synthesized, by adding another monomer after completion of polymerization of some monomer. So far, several attempts have been made (for example, refer to WO 96/30421 and WO 97/18247).

[0006]

Among block copolymers, while multiblock copolymers in which many polymer blocks are bonded have characteristics of block copolymers such as thermoplastic elastomers, as well as have higher molecular weight than block copolymers of ABA type or the like, and are expected to have high strength and stability. However, it is not easy to produce such a multiblock copolymer even with the living radical polymerization method, and there have hardly been any reports.

[0007]

[Subject which the Invention is to Solve]

The present invention has for its object to provide a multiblock copolymer composed of any of various polymers and a vinyl polymer produced by an easy production method without requiring optimization of polymerization conditions which is difficult to achieve.

[0008]

[Means for Solving the Problems]

The present invention relates to a multiblock copolymer which is produced by adding a polymer (I) containing an alkenyl group at one terminus and a group serving as an initiator group

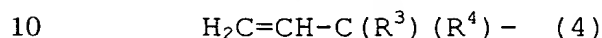
for atom transfer polymerization at the other terminus to an atom transfer radical polymerization system.

[0009]

The terminal alkenyl group is preferably a group
5 represented by the general formula 1, and more preferably a group represented by the general formula 4:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms)

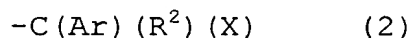


(wherein R^3 and R^4 may be the same or different and each represents a hydrogen atom or a monovalent organic group).

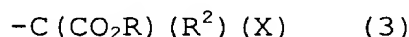
In the general formula 1, R^1 is preferably hydrogen.

[0010]

15 The group serving as an initiator group for the atom transfer radical polymerization of the polymer (I) is preferably a group represented by the general formula 2 or a group represented by the general formula 3:



20 (wherein Ar is an aryl group, which may optionally have a substituent, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, and X represents chlorine, bromine or iodine)



25 (wherein Ar is an aryl group, which may optionally have a substituent, R^2 represents a hydrogen atom or a methyl group, R represents an organic group containing 1 to 20 carbon atoms, and X represents chlorine, bromine or iodine).

30 The group represented by the general formula 2 or 3 is preferably derived from a growing terminus at the time of polymerization of a styrenic monomer or an acrylic monomer by the atom transfer radical polymerization.

[0011]

35 The present inventors have found that the growing terminus of atom transfer radical polymerization is also added

to an alkenyl group with low polymerizability. The present invention uses this finding. That is, when the polymer (I) containing an alkenyl group at one terminus and a group serving as an initiator group for atom transfer polymerization at the

5 other terminus is added to an atom transfer radical polymerization system, the group serving as an initiator group starts polymerization to be a block polymer between the polymer (I) and the polymer block which is newly polymerized. Furthermore, when the growing terminus of this block polymer or an initiator other than the polymer (I) is used in combination,

10 the growing terminus of the polymer started therefrom is added to a terminal alkenyl group of the polymer (I) to be a multiblock copolymer.

[0012]

15 In the general formula 2, R^2 is preferably hydrogen.

[0013]

The main chain of polymer (I) according to the present invention is not particularly restricted but preferred are polyester polymers, polyether polymers, vinyl polymers,

20 (meth)acrylic polymers, polysiloxane polymers, polyolefin polymers and hydrocarbon polymers.

[0014]

The polymer (I) is preferably polymerized by controlled radical polymerization, more preferably by living radical

25 polymerization, and particularly preferably by atom transfer radical polymerization. The terminal group is derived from the initiator, or is introduced by functional group conversions or the like. The polymer (I) also has a characteristic for having a narrow molecular weight distribution.

30 [0015]

The multiblock copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

[0016]

35 The present invention relates to a multiblock copolymer

which is produced by adding a polymer (I) containing an alkenyl group at one terminus and a group serving as an initiator group for atom transfer radical polymerization at the other terminus to an atom transfer radical polymerization system.

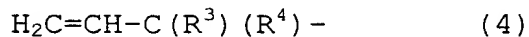
5 <<Polymer (I)>>

At first, the polymer (I) is described in the following.
<Terminus of the polymer (I)>

To an alkenyl group of the polymer (I), a growing terminus of the atom transfer polymerization is added, and the group serving as an initiator group for atom transfer polymerization serves as an initiator for atom transfer polymerization. As the result, a multiblock copolymer is produced. Therefore, the alkenyl group of the polymer (I) preferably has a terminus to which a growing terminus for atom transfer radical
10 polymerization is added but hardly undergoing polymerization, and is preferably the group represented by the general formula 1, and further preferably the group represented by the general formula 4:



20 (wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms)



(wherein R^3 and R^4 may be the same or different and each represents a hydrogen atom or a monovalent organic group).

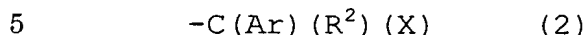
25 In the general formula 1, R^1 is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:

- $(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
- $\text{CH}(\text{CH}_2\text{CH}_3)_2$, - $\text{C}(\text{CH}_3)_2-(\text{CH}_2)_n-\text{CH}_3$, - $\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
30 - C_6H_5 , - $\text{C}_6\text{H}_5(\text{CH}_3)$, - $\text{C}_6\text{H}_5(\text{CH}_3)_2$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)$,
- $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)_2$

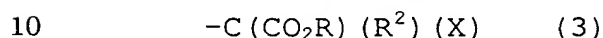
(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

35 [0017]

The group serving as an initiator group for the atom transfer radical polymerization of the polymer (I) is preferably a group represented by the general formula 2 or a group represented by the general formula 3:



(wherein Ar is an aryl group, which may optionally have a substituent, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, and X represents chlorine, bromine or iodine)



(wherein Ar is an aryl group, which may optionally have a substituent, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, R represents an organic group containing 1 to 20 carbon atoms, and X represents chlorine, bromine or iodine).

In the general formula 2, R^2 is preferably a hydrogen atom or a methyl group, and more preferably a hydrogen atom.

[0018]

Ar is an aryl group which may optionally have a substituent, and is not particularly restricted, but there may be mentioned the following groups:

20 C_6H_5- , o, m, p- $(CH_3)C_6H_4-$, 2,6- $(CH_3)_2C_6H_3-$, 2,4- $(CH_3)_2C_6H_3-$,
2,4,6- $(CH_3)_3C_6H_2-$, o, m, p- ClC_6H_4- , 2,6- $Cl_2C_6H_3-$, 2,4- $Cl_2C_6H_3-$,
2,4,6- $Cl_3C_6H_2-$, o, m, p-(tert- C_4H_9) C_6H_4- , o, m, p-(CH_3O) C_6H_4- , Np-
25 (Np is a naphthyl group).

(X represents chlorine, bromine or iodine, and preferably chlorine or bromine).

<Main chain of polymer (I)>

30 The main chain of polymer (I) according to the present invention is not particularly restricted but includes polyester polymers, polyether polymers, vinyl polymers, (meth)acrylic polymers, polysiloxane polymers, polyolefin polymers, hydrocarbon polymers, polycarbonate polymers, polyarylate polymers, diallyl phthalate polymers, polyamide polymers and
35 polyimide polymers, among others. Preferred are polyester

polymers, polyether polymers, vinyl polymers, (meth)acrylic polymers, polysiloxane polymers, polyolefin polymers and hydrocarbon polymers.

[0019]

- 5 When the main chain of the polymer (I) is a vinyl polymer, the vinyl monomer constituting the polymer is not particularly restricted and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, 10 isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl 15 (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxypropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl 20 (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 25 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl 30 (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, α -methylstyrene, chlorostyrene, styrenesulfonic acid and salts thereof; fluorine-containing vinyl monomers such as perfluoroethylene, perfluoropropylene and vinylidene 35 fluoride; silicon-containing vinyl monomers such as

vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide, 5 methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide 10 group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, 15 allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products. More preferred are acrylic acid ester monomers and methacrylic acid 20 ester monomers, and still more preferred are butyl acrylate monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers and, on that occasion, the content of such preferred monomer is preferably 40% on the weight basis. The term (meth)acrylic 25 acid employed hereinabove means acrylic acid and/or methacrylic acid.

[0020]

The molecular weight distribution, namely the ratio of weight average molecular weight (M_w) to number average 30 molecular weight (M_n) (M_w/M_n) in the polymer (I) is not particularly restricted. However, the molecular weight distribution is preferably narrow for controlling the physical property of the generated multiblock copolymer. The value of the molecular weight distribution is preferably less than 1.8, 35 more preferably not more than 1.7, still more preferably not

more than 1.6, much more preferably not more than 1.5, in particular not more than 1.4, most preferably not more than 1.3. The molecular weight distribution is most generally determined by gel permeation chromatography (GPC) using chloroform or THF as mobile phase and a polystyrene gel column. The number average molecular weight or the like can be expressed in terms of polystyrene equivalent. For producing such polymer (I) having a narrow molecular weight distribution, it is preferable to use living polymerization such as living anionic polymerization, living cationic polymerization, and living radical polymerization.

<The method of polymerizing the polymer (I)>

The polymerization method for producing the polymer (I) is not particularly restricted. Said polymer can be synthesized by various techniques of polymerization such as anionic polymerization, cationic polymerization, radical polymerization, coordination polymerization, group transfer polymerization, condensation polymerization and ring opening polymerization. Among them, living polymerization, such as living anionic polymerization, living cationic polymerization and living radical polymerization, are preferred since it is preferred that the molecular weight and molecular weight distribution be controlled and the introduction of the terminal group is easy. Among these, atom transfer radical polymerization is particularly preferred. The atom transfer radical polymerization is described below in detail.

<Terminal alkenyl group introduction>

Various techniques so far proposed can be used for introducing an alkenyl group, preferably a group of the general formula 1, into a polymer. Specific examples are given below under [A] to [C] mainly in relation to vinyl polymers producible by atom transfer radical polymerization. These, however, have no limitative meaning. As for other polymers, they can be synthesized by generally known methods, and the hydroxyl conversion method, for instance, among the methods mentioned

below can also be utilized.

[A] Method comprising introducing an alkenyl group directly into the polymer main chain on the occasion of synthesizing a vinyl polymer by radical polymerization.

5 [B] Method comprising using a vinyl polymer having at least one halogen atom and converging this halogen atom to an alkenyl-containing functional group.

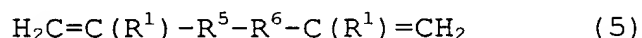
[C] Method comprising using a vinyl polymer having at least one hydroxyl group and converting this hydroxyl group to an
10 alkenyl-containing functional group.

[0021]

The above synthesis method [A] for introducing an alkenyl group directly into the polymer main chain is not particularly restricted but, specifically, there may be mentioned the
15 following methods [A-a] and [A-b], among others.

[0022]

[A-a] Method comprising subjecting, in synthesizing a vinyl polymer by living radical polymerization, a compound having a polymerizable alkenyl group and an alkenyl group low
20 in polymerizability in one and the same molecule as represented by the general formula 5:



(wherein R^1 is as defined above and the two of them may be the same or different, R^8 represents $-\text{C}(\text{O})\text{O}-$ (ester group) or o-,
25 m- or p-phenylene group and R^9 represents a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally have one or more ether bonds; when R^5 is an ester group, said compound is a (meth)acrylate compound and, when R^5 is a phenylene group, said compound is a styrenic compound),
30 to reaction, together with a predetermined vinyl monomer.

The group R^6 in the above general formula 5 is not particularly restricted but includes, among others, alkylene groups such as methylene, ethylene and propylene; o-, m- or p-phenylene group; aralkyl groups such as benzyl; and alkylene
35 groups containing an ether bond, such as $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ and

-O-CH₂-.

[0023]

Among the compounds represented by the general formula 5, the following compounds are preferred because of their ready availability.

- $\text{H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{CH}=\text{CH}_2$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{CH}=\text{CH}_2$,
 (wherein, in each formula, n represents an integer of 0 to 20);
 $\text{H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH}=\text{CH}_2$,
 10 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH}=\text{CH}_2$,

wherein, in each formula, n represents an integer of 0 to 20, and m represents an integer 0 to 20;

- o-, m-, p-divinylbenzene,
 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}=\text{CH}_2$,
 15 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$,
 20 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}=\text{CH}_2$,
 25 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OCH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$,
 o-, m-, p- $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$,

in the above formulas, C₆H₄ denotes a phenylene group.

[0024]

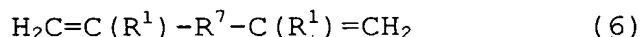
- The time for subjecting said compound having a
 30 polymerizable alkenyl group and an alkenyl group low in
 polymerizability combinedly is not particularly restricted but
 it is preferred that the second monomer be subjected to reaction
 at the terminal stage of polymerization reaction or after
 completion of the polymerization of the predetermined monomer.

35 [0025]

[A-b] Method comprising subjecting a compound having at least two alkenyl groups low in polymerizability as the second monomer to reaction at the terminal stage of polymerization reaction or after completion of the reaction of the
 5 predetermined monomer in vinyl polymer synthesis by living radical polymerization.

[0026]

As such compound, which is not particularly restricted, there may be mentioned compounds represented by the general
 10 formula 6:



wherein R^1 is as defined above and the two of them groups may be the same or different and R^6 represents a divalent organic group having 1 to 20 carbon atoms which may optionally contain
 15 one or more ether bonds.

[0027]

The compound of the above general formula 6 is not particularly restricted but is preferably a 1,5-hexadiene, 1,7-octadiene or 1,9-decadiene for reasons of ready
 20 availability.

[0028]

As regards the above method [A] for synthesizing a vinyl polymer having at least one alkenyl group by introducing the alkenyl group directly into the polymer main chain, the method
 25 [A-b] is preferred since it is more easy to control the number of alkenyl groups to be introduced per polymer molecule.

[0029]

In the above method [B] for synthesizing a vinyl polymer having a terminal halogen, the atom transfer radical
 30 polymerization method is preferably used. The method of substituting the halogen in said polymer to an alkenyl-containing functional group is not particularly restricted but includes, among others, the techniques [B-a] to [B-d] specifically mentioned below.

35 [0030]

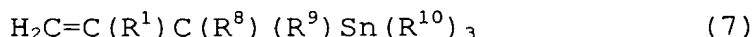
[B-a] Method comprising substituting the halogen by reacting a terminal halogen-containing vinyl polymer with one of various alkenyl-containing organometallic compounds.

[0031]

5 As such organometallic compounds, there may be mentioned organolithium, organosodium, organopotassium, organomagnesium, organotin, organosilicon, organozinc and organocopper compounds, among others. In particular, organotin and organocopper compounds are preferred, since they
10 react selectively with the halogen at the growing terminus in atom transfer radical polymerization but are low in reactivity with the carbonyl group.

[0032]

Preferred as the alkenyl-containing organotin compound, 15 which is not particularly restricted, are compounds represented by the general formula 7:



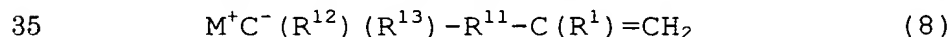
(wherein R^1 is as defined above, R^{81} and R^{92} may be the same or different and each represents a hydrogen atom or an alkyl group
20 having 1 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms or an aralkyl group having 7 to 10 carbon atoms and R^{10} represents an alkyl group having 1 to 10 carbon atoms, an aryl group or an aralkyl group).

[0033]

25 Specific examples of the organotin compound of the general formula 7 are allyltributyltin, allyltrimethyltin, allyltri(n-octyl)tin, allyltri(cyclohexyl)tin and the like. As the alkenyl-containing organocopper compound, there may be mentioned divinylcopper lithium, diallylcopper lithium,
30 diisopropenylcopper lithium and the like.

[0034]

[B-b] Method comprising reacting a halogen-terminated vinyl polymer with an alkenyl-containing stabilized carbanion represented by the general formula 8, for instance:



(wherein R^1 is as defined above, R^{11} represents a divalent organic group having 1 to 20 carbon atoms, which may optionally containing one or more ether groups, R^{12} and R^{13} each is an electron-withdrawing group contributing to stabilize the carbanion C^- or one of them is said electron-withdrawing group and the other is a hydrogen atom or an alkyl group having 1 to 10 carbon atoms or a phenyl group. As the electron-withdrawing group represented by R^{12} and R^{13} , there may be mentioned $-CO_2R$ (ester group), $-C(O)R$ (keto group), $-CON(R)_2$ (amide group), $-COSR$ (thioester group), $-CN$ (nitrile group) and $-NO_2$ (nitro group), among others. The substituent R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, preferably an alkyl group having 1 to 10 carbon atoms or a phenyl group. Particularly preferred as R^{12} and R^{13} are $-CO_2R$, $-C(O)R$ and $-CN$. M^+ represents an alkali metal ion or a quaternary ammonium ion).

As the alkali metal ion, there may specifically be mentioned lithium ion, sodium ion and potassium ion and, as the quaternary ammonium ion, there may specifically be mentioned tetramethylammonium ion, tetraethylammonium ion, trimethylbenzylammonium ion, trimethyldodecylammonium ion and tetrabutylammonium ion, among others.

[0035]

The carbanion of the above general formula 8 can be obtained by reacting a precursor thereof with a basic compound and thereby withdrawing an active carbon.

[0036]

As example of the compound to serve as the precursor of the carbanion of the general formula 8, there may be mentioned the following:

$H_2C=CH-CH(CO_2CH_3)_2$, $H_2C=CH-CH(CO_2C_2H_5)_2$,
 $H_2C=CH-(CH_2)_nCH(CO_2CH_3)_2$, $H_2C=CH-(CH_2)_nCH(CO_2C_2H_5)_2$,
 o-, m-, p- $H_2C=CH-C_6H_4-CH(CO_2CH_3)_2$,
 o-, m-, p- $H_2C=CH-C_6H_4-CH(CO_2C_2H_5)_2$,
 o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH(CO_2CH_3)_2$,

- $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(CO}_2\text{C}_2\text{H}_5)_2$,
 $\text{H}_2\text{C=CH-CH(C(O)CH}_3\text{)(CO}_2\text{C}_2\text{H}_5)$, $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{CH(C(O)CH}_3\text{)(CO}_2\text{C}_2\text{H}_5)$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH(C(O)CH}_3\text{)(CO}_2\text{C}_2\text{H}_5)$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(C(O)CH}_3\text{)(CO}_2\text{C}_2\text{H}_5)$,
5 $\text{H}_2\text{C=CH-CH(C(O)CH}_3\text{)}_2$, $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{CH(C(O)CH}_3\text{)}_2$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH(C(O)CH}_3\text{)}_2$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(C(O)CH}_3\text{)}_2$,
 $\text{H}_2\text{C=CH-CH(CN)(CO}_2\text{C}_2\text{H}_5)$, $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{CH(CN)(CO}_2\text{C}_2\text{H}_5)$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH(CN)(CO}_2\text{C}_2\text{H}_5)$,
10 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(CN)(CO}_2\text{C}_2\text{H}_5)$, $\text{H}_2\text{C=CH-CH(CN)}_2$,
 $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{CH(CN)}_2$, $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH(CN)}_2$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(CN)}_2$, $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{NO}_2$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{NO}_2$, $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH}_2\text{NO}_2$,
 $\text{H}_2\text{C=CH-CH(C}_6\text{H}_5\text{)(CO}_2\text{C}_2\text{H}_5)$, $\text{H}_2\text{C=CH-(CH}_2\text{)}_n\text{CH(C}_6\text{H}_5\text{)(CO}_2\text{C}_2\text{H}_5)$,
15 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH(C}_6\text{H}_5\text{)(CO}_2\text{C}_2\text{H}_5)$,
 $\text{o-, m-, p-H}_2\text{C=CH-C}_6\text{H}_4\text{-CH}_2\text{CH(C}_6\text{H}_5\text{)(CO}_2\text{C}_2\text{H}_5)$,
in the above formulas, n represents an integer of 1 to 10.

[0037]

For preparing the carbanion of the general formula 8 by
 withdrawing proton from the above compound, various basic
 compounds can be used. As examples of such basic compounds,
 there may be mentioned the following compounds:

Alkali metals such as sodium, potassium and lithium;
 metal alkoxides such as sodium methoxide, potassium methoxide,
 25 lithium methoxide, sodium ethoxide, potassium ethoxide,
 lithium ethoxide, sodium tert-butoxide and potassium
 tert-butoxide; carbonates such as sodium carbonate, potassium
 carbonate, lithium carbonate and sodium hydrogencarbonate;
 hydroxides such as sodium hydroxide and potassium hydroxide;
 30 hydrides such as sodium hydride, potassium hydride,
 methyllithium and ethyllithium; organometals such as
 n-butyllithium, tert-butyllithium, lithium diisopropylamide
 and lithium hexamethyldisilazide; alkylamines such as
 trimethylamine, triethylamine and tributylamine; polyamines
 35 such as tetramethylethylenediamine and

pentamethyldiethylenetriamine; pyridine compounds such as pyridine and picoline; and so forth.

The basic compound is used in an equivalent amount or in slight excess, preferably 1 to 1.2 equivalent, relative to the precursor substance.

[0038]

A quaternary ammonium salt can also be used as said carbanion. In that case, it can be obtained by preparing a carboxylic acid alkali metal salt and reacting this with a quaternary ammonium halide. Examples of the quaternary ammonium halide are tetramethylammonium halides, tetraethylammonium halides, trimethylbenzylammonium halides, trimethyldodecylammonium halides and tetrabutylammonium halides, among others.

[0039]

As the solvent to be used in reacting the above precursor compound with the basic compound, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether, tetrahydrofuran, diphenyl ether, anisole and dimethoxybenzene; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and t-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate solvents such as ethylene carbonate and propylene carbonate; amide solvents such as dimethylformamide and dimethylacetamide; and sulfoxide solvents such as dimethyl sulfoxide. These may be used singly or two or more of them may be used in admixture.

[0040]

The carbanion represented by the general formula 8 as prepared by reacting the above precursor with the basic compound is reacted with a halogen-terminated vinyl polymer, whereby an

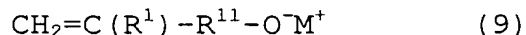
alkenyl-terminated vinyl polymer can be obtained. [B-c]
 Method comprising reacting a halogen-terminated vinyl polymer
 with an elementary metal or an organometallic compound to
 convert the former to an enolate anion, followed by reaction
 5 with an alkenyl-containing electrophilic compound.

[0041]

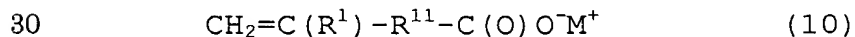
Particularly preferred as the elementary metal is zinc,
 since it hardly causes such a side reaction as the attack of
 the resulting enolate anion against other ester groups or the
 10 transition thereof. Usable as the alkenyl-containing
 electrophilic compound are various ones such as, for example,
 alkenyl-containing compounds having a leaving group such as a
 halogen atom or an acetyl group, alkenyl-containing carbonyl
 compounds, alkenyl-containing isocyanate compounds and
 15 alkenyl-containing acid halides. Among these,
 alkenyl-containing compounds having a leaving group such as a
 halogen atom or an acetyl group are preferred since the use
 thereof does not allow introduction of atoms other than a carbon
 atom into the main chain, hence the weathering resistance of
 20 the vinyl polymer is not lost.

[0042]

[B-d] Method comprising reacting a halogen-terminated
 vinyl polymer with an alkenyl-containing oxy anion represented
 by the general formula 9 shown below or an alkenyl-containing
 25 carboxylate anion represented by the general formula 10 given
 below, to thereby cause substitution of the alkenyl-containing
 substituent for the halogen atom:



(wherein R^1 , R^{11} and M^+ are as defined above);



(wherein R^1 , R^{11} and M^+ are as defined above).

As the precursor compounds of the oxy anions represented
 by the general formulas 9 and 10, there may be mentioned the
 following compounds, among others:
 35 alcoholic hydroxyl-containing compounds such as

- $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{CH}_3)-\text{OH}$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{OH}$,
 $\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_n-\text{OH}$ (n represents an integer 2 to 20),
 $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_2-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{C}(\text{O})\text{O}-(\text{CH}_2)_2-\text{OH}$,
 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(\text{O})\text{O}-(\text{CH}_2)_2-\text{OH}$, $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$,
5 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$,
 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$ and the like;
phenolic hydroxyl-containing compounds such as
 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$, $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$,
 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{OH}$ and the like;
10 carboxyl-containing compounds such as $\text{H}_2\text{C}=\text{CH}-\text{C}(\text{O})-\text{OH}$,
 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(\text{O})-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}(\text{O})-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_n-\text{C}(\text{O})-\text{OH}$
(n represents an integer 2 to 20),
 $\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_n-\text{OC}(\text{O})-(\text{CH}_2)_m-\text{C}(\text{O})-\text{OH}$ (m and n are the same or
different, each represents an integer of 0 to 19),
15 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$, $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$,
 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$,
 $o-, m-, p-\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_n-\text{OC}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$ (n represents an
integer 0 to 13) and the like.

[0043]

- 20 Various basic compounds are used to withdraw a proton from
the above compounds and convert it to an anion of the above
general formula 9 or 10. Those basic compounds specifically
mentioned hereinabove as useful in preparing the carbanion of
the general formula 8 are all usable as the above basic compounds.
25 As regards the reaction solvent, all those specifically
mentioned hereinabove in relation to carbanion preparation are
suited for use.

[0044]

- Among the above synthesis methods [B], the method [B-d]
30 is preferred for alkenyl group introduction by converting the
halogen in a halogen-terminated vinyl polymer obtained by atom
transfer radical polymerization using an organic halide or
halogenated sulfonyl compound or the like as an initiator and
a transition metal complex as a catalyst to an alkenyl group,
35 since the alkenyl group introduction can be realized with a high

proportion. Among the variations of method [B-d], the one comprising subjecting an alkenyl-containing carboxylate anion represented by the general formula 10 to reaction is more preferred.

5 [0045]

When, in the method of producing a vinyl monomer which comprises the atom transfer radical polymerization method using an organic halide or halogenated sulfonyl compound or the like as an initiator and a transition metal complex as a catalyst, 10 the alkenyl-containing organic halide is used as an initiator, a vinyl polymer having a structure such that the alkenyl group occurs at one terminal and the initiator group for atom transfer radical polymerization at the other terminus can be obtained. When the halogen atom at the termination terminus of the polymer 15 thus obtained is converted to an alkenyl-containing substituent, a vinyl polymer having an alkenyl group at both ends can be obtained. Usable as the method for said conversion is the method already described hereinabove.

[0046]

20 Detailed mention of the alkenyl-containing organic halide will be made later herein in relation to the explanation of atom transfer radical polymerization.

[0047]

The method of substituting an alkenyl-containing 25 functional group for the hydroxyl group of a hydroxyl-terminated vinyl polymer according to the synthesis method [C] mentioned above is not particularly restricted but there may be mentioned those specific methods [C-a] to [C-d] which are to be mentioned below.

30 [0048]

The above hydroxyl-terminated vinyl polymer can be obtained by the methods [D-a] to [D-f] to be mentioned later herein.

[0049]

35 [C-a] Method comprising reacting the hydroxyl group of

a hydroxyl-terminated vinyl polymer with a base such as sodium hydroxide or sodium methoxide and then reacting the resulting product with an alkenyl-containing halide such as allyl chloride.

5 [0050]

[C-b] Method comprising reacting a hydroxyl-terminated vinyl polymer with an alkenyl-containing isocyanate compound such as allyl isocyanate.

[0051]

10 [C-c] Method comprising reacting a hydroxyl-terminated vinyl polymer with an alkenyl-containing acid halide, such as (meth)acryloyl chloride, in the presence of a base such as pyridine.

[0052]

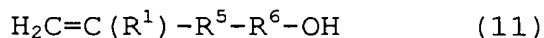
15 [C-d] Method comprising reacting a hydroxyl-terminated vinyl polymer with an alkenyl-containing carboxylic acid, such as acrylic acid, in the presence of an acid catalyst.

[0053]

20 The method of producing the hydroxyl-terminated vinyl polymer to be used for the above method [C] includes, but is not limited to, such methods as mentioned below under [D-a] to [D-f].

[0054]

25 [D-a] Method comprising subjecting a compound having both a polymerizable alkenyl group and a hydroxyl group in one and the same molecule as represented by the general formula 11 shown below to reaction as a second monomer on the occasion of synthesizing a vinyl polymer by living radical polymerization:



30 (wherein R^1 , R^5 and R^6 are as defined above.)

The time for subjecting the compound having both a polymerizable alkenyl group and a hydroxyl group in one and the same molecule to reaction is not restricted but, particularly when rubber-like properties are expected, said compound is
35 preferably subjected to reaction as a second monomer at the

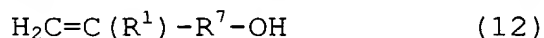
terminal stage of the polymerization reaction or after completion of the reaction of a predetermined monomer.

[0055]

[D-b] Method comprising subjecting a compound having an alkenyl group low in polymerizability and a hydroxyl group in one and the same molecule to reaction as a second monomer on the occasion of synthesizing a vinyl polymer by living radical polymerization at the terminal stage of the polymerization reaction or after completion of the reaction of a predetermined monomer.

[0056]

Such compound is not particularly restricted but includes, for example, compounds represented by the general formula 12:

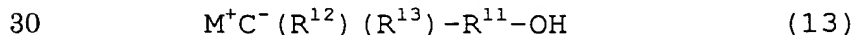


(wherein R^1 and R^7 are as defined above.)

Said compounds of the general formula 12 are not particularly restricted but, from the viewpoint of ready availability, such alkenyl alcohols as 10-undecenol, 5-hexenol and allyl alcohol are preferred.

[D-c] Method comprising hydrolyzing the halogen atom of a vinyl polymer having a terminal carbon-halogen bond as obtained by atom transfer radical polymerization, as disclosed in Japanese Kokai Publication Hei-04-132706, or reacting said halogen atom with a hydroxyl-containing compound to thereby introduce a hydroxyl group terminally.

[D-d] Method comprising reacting a vinyl polymer having a terminal carbon-halogen bond as obtained by atom transfer radical polymerization with a hydroxyl-containing stabilized carbanion represented by the general formula 13:



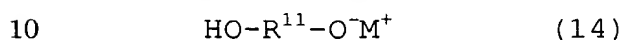
(wherein R^{11} , R^{12} and R^{13} are as defined above), to thereby effect substitution for the halogen.

[D-e] Method comprising reacting a vinyl polymer having a terminal carbon-halogen bond as obtained by atom transfer radical polymerization with an elementary metal, such as zinc,

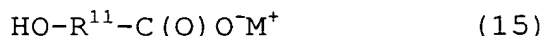
or an organometallic compound and then reacting the resulting enolate anion with an aldehyde or ketone.

[0057]

[D-f] Method comprising reacting a halogen-terminated
5 vinyl polymer with a hydroxyl-containing oxy anion represented by the general formula 14 given below or a hydroxyl-containing carboxylate anion represented by the general formula 15 shown below to thereby substitute the corresponding hydroxyl-containing substituent for the halogen:



(wherein R^1 , R^{11} and M^+ are as defined above);



(wherein R^1 , R^{11} and M^+ are as defined above).

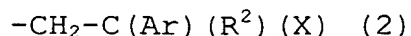
In cases where, in the practice of the present invention,
15 the hydroxyl introduction is free of direct halogen involvement, such as in [D-a] and [D-b], the method [D-b] is more preferred since the control is easier.

[0058]

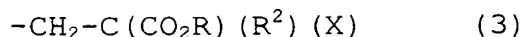
In cases where the hydroxyl group introduction is
20 effected by converting the halogen atom of a vinyl polymer having at least one carbon-halogen bond represented by the general formula (2), such as in [D-c] to [D-f], the method [D-f] is more preferred since the control is easier.

<Introduction of an initiator group for atom transfer radical
25 polymerization>

The initiator group for atom transfer radical polymerization has the structure of the initiator mentioned in detail hereinabove in the description of atom transfer radical polymerization and is preferably a group represented by the
30 general formula 2 or 3, a benzyl halide group or a sulfonyl halide group, for instance:



(wherein Ar is an aryl group, which may optionally have a substituent, R^2 is a hydrogen atom or a hydrocarbon group having
35 1 to 20 carbon atoms and X is chlorine, bromine or iodine);



(wherein Ar is an aryl group, which may optionally have a substituent, R^2 is a hydrogen atom or a methyl group, R is an organic group having 1 to 20 carbon atoms and X is chlorine, bromine or iodine).

When the polymer (I) is produced by atom transfer radical polymerization, the terminus thereof is an initiator group for atom transfer radical polymerization. The group represented by the general formula 2 or 3 is preferably obtained as a growing terminus when a styrenic or acrylic monomer is polymerized by atom transfer radical polymerization. When this initiator group is subjected to conversion for alkenyl group introduction, as mentioned hereinabove, there can be mentioned the method comprising producing a polymer having a growth terminus at both ends by using a bifunctional initiator, for instance, and converting only one terminus to an alkenyl group.

As another method, there may be mentioned the method of introducing a compound having an initiator group for atom transfer radical polymerization and an alkenyl group, or a compound having an initiator group for atom transfer radical polymerization and a hydrosilyl group into various hydrosilyl- or alkenyl-containing polymers by hydrosilylation (refer to Polymer, 39 (21), 5163 (1998)).

[0059]

Although the method of producing the above-mentioned polymer (I) is not particularly restricted, a preferred method comprises conducting atom transfer radical polymerization using a functional group-containing initiator and using the product as it is when the functional group is an alkenyl group and, when the functional group is other than an alkenyl group, converting said group to an alkenyl group. As an example, the method described in Polymer J., 30, 138 (1998) may be mentioned.

<<Method of producing a multiblock copolymer>>

In the following, a method of producing a multiblock copolymer which comprises adding a polymer (I) containing an

alkenyl group at one terminus and a group serving as an initiator group for atom transfer polymerization at the other terminus to an atom transfer radical polymerization system.

<As for atom transfer radical polymerization>

5 In its narrow sense, the term "living polymerization" means that polymerization in which the molecular chain grows while a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which molecules grow while terminally
10 inactivated molecules and terminally activated ones are in equilibrium. The latter definition is to be applied to the present invention. "Living radical polymerization methods" have recently been aggressively investigated by a number of groups. As examples, there may be mentioned, among others, the
15 method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an
20 organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. The living radical polymerization hardly undergo termination reaction and give polymers narrow in molecular weight distribution (M_w/M_n being about 1.1 to 1.5) and the molecular weight can arbitrarily be
25 controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization regarded as difficult to control because of a high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other, among others.

30 [0060]

 "Living radical polymerization methods", which enable introduction of a specific functional group-containing monomer into a polymer at a substantially arbitrary site thereof in addition to obtaining polymers with a narrow molecular weight
35 distribution and a low viscosity on its properties, are more

preferred as methods of producing the specific functional group-containing vinyl polymers.

[0061]

Among such "living radical polymerization methods", the
 5 "atom transfer polymerization methods" for polymerizing vinyl monomers using an organic halide, sulfonyl halide or the like as an initiator and a transition metal complex as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614;
 10 Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; WO 96/30421; WO 97/18247; WO 98/01480; WO 98/40415; Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721; Japanese Kokai Publication Hei-09-208616; and Japanese Kokai Publication Hei-08-41117) are more preferred as the
 15 method of producing specific functional group-containing vinyl polymers, since, in addition to the characteristic features of the above-mentioned "living radical polymerization methods", halogen, etc., relatively favorable for functional group conversion reactions is contained at its terminus and the degree
 20 of freedom is high in designing the initiator or catalyst. In the practice of the present invention, the atom transfer radical polymerization is used.

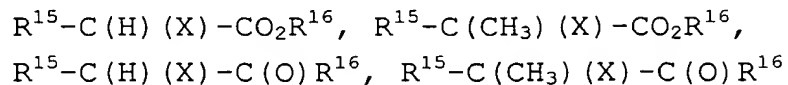
In this atom transfer radical polymerization, an organic halide, in particular an organic halide having a highly reactive
 25 carbon-halogen bond (e.g. a carbonyl compound having a halogen in α -position or a compound having a halogen at the benzyl site), or a sulfonyl halide compound is used as an initiator. As shown by the term "atom transfer radical polymerization", a halogen group derived from an initiator is generally present at a
 30 growing terminus of the polymer.

<Initiator for atom transfer radical polymerization>

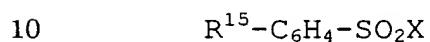
The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:

35 $C_6H_5-CH_2X$, $C_6H_5-C(H)(X)CH_3$, $C_6H_5-C(X)(CH_3)_2$

(in the above chemical formulas, C_6H_5 is a phenyl group and X is chlorine, bromine or iodine);



5 (in which R^{15} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and R^{16} represents a monovalent organic group having 1 to 20 carbon atoms); and



(in which R^{15} is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

15 [0062]

In the practice of the present invention, a polymer (I) containing an alkenyl group at one terminus and a group serving as an initiator group for atom transfer polymerization at the other terminus is added to an atom transfer radical

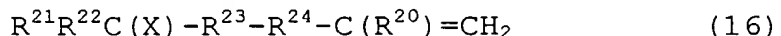
20 polymerization system. Since the initiator group of the polymer (I) can start atom transfer radical polymerization, another initiator is not necessary.

[0063]

25 Furthermore, when an organic halide or sulfonyl halide having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among
30 others. This method can be applied to synthesize the polymer (I). Moreover, in the practice of the present invention, atom transfer radical polymerization is carried out by using an initiator containing such functional groups, a multiblock copolymer containing various functional groups at its terminus
35 can be obtained.

[0064]

When an alkenyl-containing initiator is used, the polymer containing the group represented by the general formula 1 can be easily obtained. The alkenyl-containing organic halide is not restricted but may be one having the structure shown by the general formula 16:



(wherein R^{20} is a hydrogen atom or a methyl group, R^{21} and R^{22} each is a hydrogen atom or a monovalent alkyl having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and R^{21} and R^{22} may be bound to each other at respective other termini, R^{23} is $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group, R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is chlorine, bromine or iodine).

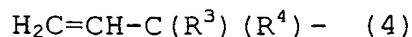
In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

[0065]

As specific examples of the substituents R^{21} and R^{22} , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc. R^{21} and R^{22} may be bound to each other at respective other termini to form a cyclic skeleton. In such case, $-R^{21}-R^{22}-$ may be, for example, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$ and the like.

[0066]

The alkenyl group preferably has a terminus to which a growing terminus of the atom transfer radical polymerization is added but hardly undergoing polymerization as mentioned above, and preferred is a group represented by the general formula 4:



(wherein R^3 and R^4 may be the same or different and each represents a hydrogen atom or a monovalent organic group).

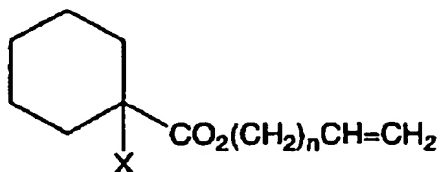
[0067]

As specific examples of the alkenyl-containing organic halide represented by the general formula 16, there may be mentioned the following:

- 5 $XCH_2C(O)O(CH_2)_nCH=CH_2$,
 $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$,
 $(H_3C)_2C(X)C(O)O(CH_2)_nCH=CH_2$,
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nCH=CH_2$

[0068]

- 10 [Chemical 1]

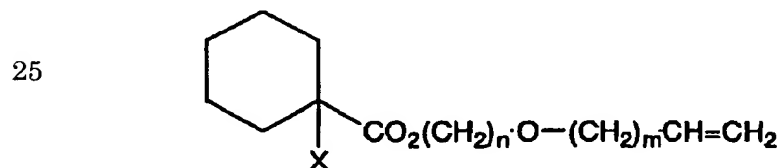


- 15 (in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20, n is preferably an integer of 1 to 20);

- $XCH_2C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,
 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,
 20 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,

[0069]

[Chemical 2]

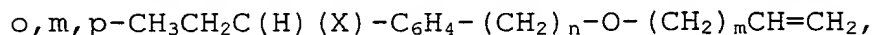
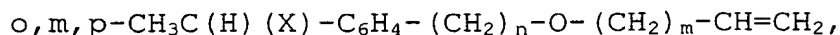
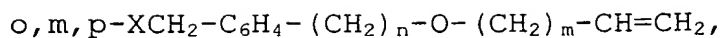


- (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20; m is preferably an integer of 1 to 20);

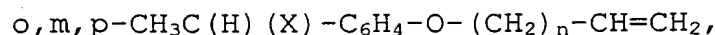
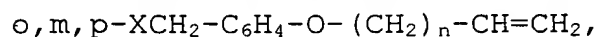
- 30 $o, m, p-XCH_2-C_6H_4-(CH_2)_n-CH=CH_2$,
 $o, m, p-CH_3C(H)(X)-C_6H_4-(CH_2)_n-CH=CH_2$,
 $o, m, p-CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_n-CH=CH_2$,

- (in the above formulas, X is chlorine, bromine or iodine and
 35 n is an integer of 0 to 20; n is preferably an integer of 1 to

20);

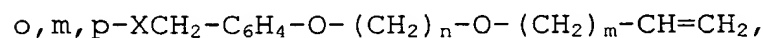


- 5 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20; m is preferably an integer of 1 to 20);

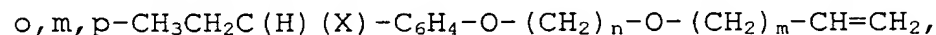


- 10 $o, m, p\text{-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2\text{)}_n\text{-CH=CH}_2,$

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20; n is preferably an integer of 1 to 20);

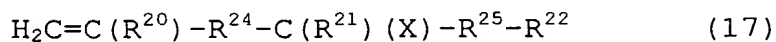


- 15 $o, m, p\text{-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2\text{)}_n\text{-O-(CH}_2\text{)}_m\text{-CH=CH}_2,$



(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20 and m is an integer of 0 to 20).

- As the alkenyl-containing organic halide, there may
20 further be mentioned compounds represented by the general
formula 17:

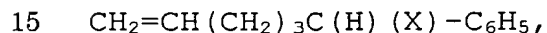
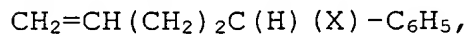
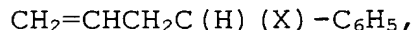
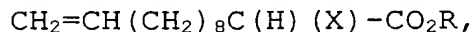
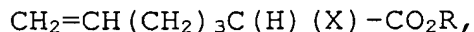
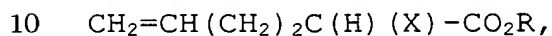
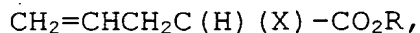
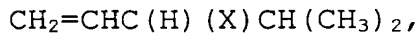
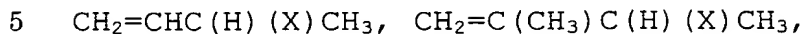


- (wherein R^{20} , R^{21} , R^{22} , R^{24} and X are defined above and R^{25} is a
direct bond, -C(O)O- (ester group), -C(O)- (keto group) or an
25 o -, m - or p -phenylene group).

- R^{24} is a direct bond or a divalent organic group having
1 to 20 carbon atoms (which may contain one or more ether bonds)
and, when it is a direct bond, the vinyl group is bound to the
carbon to which the halogen is bound, to form an allyl halide.
30 In this case, the carbon-halogen bond is activated by the
neighboring vinyl group, so that it is not always necessary for
 R^{25} to be a C(O)O group or a phenylene group, for instance, but
it may be a direct bond. When R^{24} is not a direct bond, R^{25} is
preferably a C(O)O group, C(O) group or phenylene group so that
35 the carbon-halogen bond may be activated.

[0070]

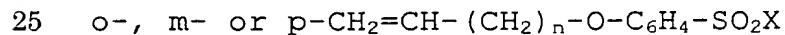
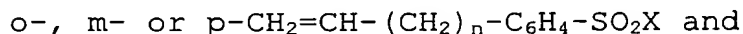
As a specific example of compounds represented by the general formula 17, there can be mentioned,



(in the above formulas, X is chlorine, bromine or iodine, and R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms). Among these, allyl chloride and allyl
20 bromide are preferred from cost and availability viewpoint.

[0071]

Specific examples of the alkenyl-containing sulfonyl halide are as follows:



(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20; n is preferably an integer of 1 to 20), among others.

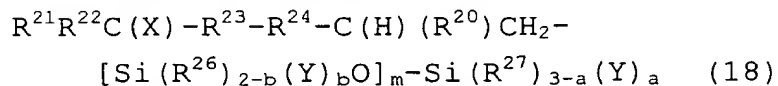
[0072]

30 When an alkenyl-containing initiator is used, care should be taken since there is a possibility that olefin of the initiator may also react with the polymerization terminus.

[0073]

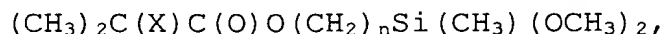
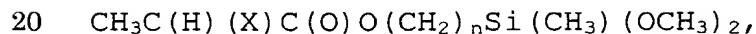
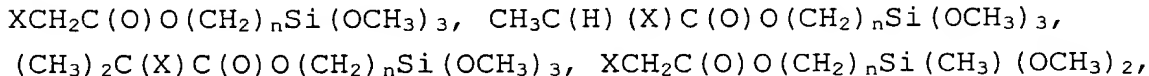
35 The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, those

having a structure shown by the general formula 18:

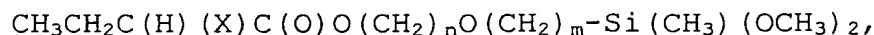
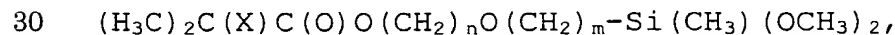
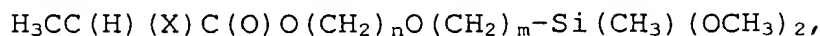
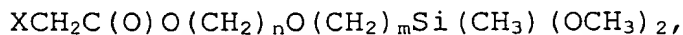
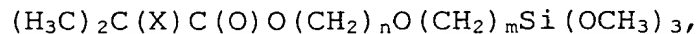
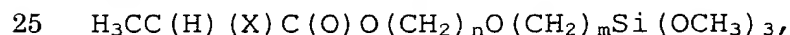
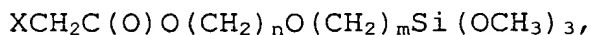


(wherein R^{20} , R^{21} , R^{22} , R^{23} , R^{24} and X are as defined above, R^{26} and R^{27} each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented by $(R')_3SiO-$ (in which R' is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R^{26} and/or R^{27} groups, they may be the same or different, Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different, a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation $a+mb \geq 1$ should be satisfied.

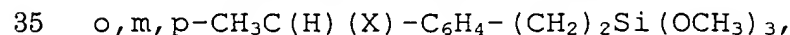
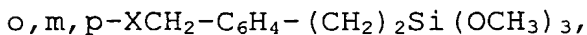
As a specific example of compounds represented by the general formula 18, there can be mentioned,



(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20),

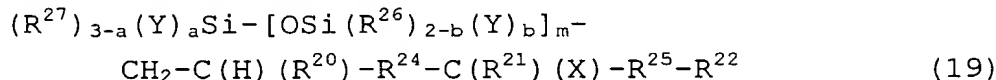


(wherein, in each formula, X is chlorine, bromine or iodine, n is an integer of 0 to 20, and m is an integer of 0 to 20),



- o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₂Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₃Si(OCH₃)₃,
 5 o, m, p-XCH₂-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)₃Si(OCH₃)₃,
 10 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-XCH₂-C₆H₄-O-(CH₂)₂-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃Si(OCH₃)₃,
 (wherein, in each formula, X is chlorine, bromine or iodine).

- 15 As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 19:



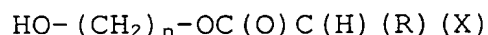
- 20 (wherein R²⁰, R²¹, R²², R²⁴, R²⁵, R²⁶, R²⁷, a, b, m, X and Y are as defined above).

As a specific example of such compounds, there can be mentioned;

- (CH₃O)₃SiCH₂CH₂C(H)(X)C₆H₅, (CH₃O)₂(CH₃)SiCH₂CH₂C(H)(X)C₆H₅,
 25 (CH₃O)₃Si(CH₂)₂C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₂C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₄C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₉C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₉C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-C₆H₅,
 30 (CH₃O)₃Si(CH₂)₄C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-C₆H₅,
 (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

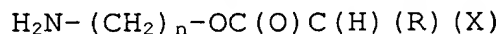
- 35 [0074]

The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



5 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide
10 is not particularly restricted but includes compounds represented by the following formula:

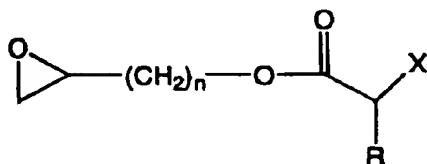


(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl having
15 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The epoxy-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

20 [0075]

[Chemical 3]



25

(wherein X represents chlorine, bromine or iodine, R represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group
30 containing 7 to 20 carbon atoms and n is an integer of 1 to 20).

In the atom transfer radical polymerization method, when an organic halide or sulfonyl halide having two or more initiation sites is used as an initiator, a polymer having two or more growing termini is obtained. Specific example thereof
35 include the following:

o, m, p-XCH₂-C₆H₄-CH₂X, o, m, p-CH₃C(H)(X)-C₆H₄-C(H)(X)CH₃, o, m, p-(CH₃)₂C(X)-C₆H₄-C(X)-(CH₃)₂

(wherein C₆H₄ represents a phenylene group, and X represents chlorine, bromine or iodine)

5 RO₂C-C(H)(X)-(CH₂)_n-C(H)(X)-CO₂R,

RO₂C-C(CH₃)(X)-(CH₂)_n-C(CH₃)(X)-CO₂R,

RC(O)-C(H)(X)-(CH₂)_n-C(H)(X)-C(O)R,

RC(O)-C(CH₃)(X)-(CH₂)_n-C(CH₃)(X)-C(O)R

(wherein R represents an alkyl group having 1 to 20 carbon atoms,

10 aryl group or aralkyl group, n represents an integer of 0 to 20, and X represents chlorine, bromine or iodine)

XCH₂-C(O)-CH₂X, H₃C-C(H)(X)-C(O)-C(H)(X)-CH₃,

(H₃C)₂C(X)-C(O)-C(X)(CH₃)₂, C₆H₅C(H)(X)-(CH₂)_n-C(H)(X)C₆H₅

(wherein X represents chlorine, bromine or iodine, and n

15 represents an integer of 0 to 20)

XCH₂CO₂-(CH₂)_n-OCOCH₂X, CH₃C(H)(X)CO₂-(CH₂)_n-OCOC(H)(X)CH₃,

(CH₃)₂C(X)CO₂-(CH₂)_n-OCOC(X)(CH₃)₂

(wherein n represents an integer of 1 to 20)

XCH₂C(O)C(O)CH₂X, CH₃C(H)(X)C(O)C(O)C(H)(X)CH₃,

20 (CH₃)₂C(X)C(O)C(O)C(X)(CH₃)₂, o-, m-, p-XCH₂CO₂-C₆H₄-OCOCH₂X,

o-, m-, p-CH₃C(H)(X)CO₂-C₆H₄-OCOC(H)(X)CH₃,

o-, m-, p-(CH₃)₂C(X)CO₂-C₆H₄-OCOC(X)(CH₃)₂

o-, m-, p-XSO₂-C₆H₄-SO₂X

(wherein X represents chlorine, bromine or iodine)

25 <Monomer>

The vinyl monomer to be used in controlled radical polymerization of the present invention is not particularly restricted and those mentioned above may be used.

<Catalyst>

30 The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably is a metal complex containing an element of the group 7, 8, 9, 10 or 11 of the periodic table as a central metal, and more
35 preferably are complexes of copper (valence: zero), monovalent

copper, divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred. Specific examples of monovalent copper compounds are cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide,
 5 cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof or a polyamine such as tetramethylethylenediamine, pentamethyldiethylenetriamine or hexamethyltris(2-aminoethyl)amine, is added to enhance the
 10 catalytic activity. A tris(triphenylphosphine) complex of divalent ruthenium chloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is also suited for use as a catalyst. When a ruthenium compound is used as a catalyst, an aluminum alkoxide is added as an activator. Furthermore, a bis(triphenylphosphine) complex of divalent iron
 15 ($\text{FeCl}_2(\text{PPh}_3)_2$), a bis(triphenylphosphine) complex of divalent nickel ($\text{NiCl}_2(\text{PPh}_3)_2$) and a bis(tributylphosphine) complex of divalent nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are also suited as catalysts.
 <Solvent and temperature>

The above-mentioned atom transfer radical polymerization
 20 can be carried out in the absence or presence of various solvents. As the solvent, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform;
 25 ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl
 30 acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture. The above polymerization can be conducted within the temperature range of room temperature to 200°C, preferably 50°C to 150°C.

35 <Addition of polymer (I)>

The time for adding the polymer (I) to the atom transfer radical polymerization system is not particularly restricted but should be adequate to the production of the desired multiblock copolymer. There may be mentioned, for example, the
5 technique already mentioned hereinabove which comprises adding it as an initiator from the initial stage of polymerization, the technique which comprises adding it during polymerization, and the technique which comprises adding it at the point of time of completion of the polymerization and adding simultaneously
10 or later the cationically polymerizable monomer again. The point of time of completion of the polymerization is preferably the time point at which not less than 90%, more preferably not less than 99% of the monomer has been polymerized. Mere addition of the polymer (I) after completion of this
15 polymerization hardly results in multiblock formation and one more addition of the radically polymerizable monomer is required. If this time of addition is too late, the growing terminus of the polymer (I) may possibly add directly to the terminus of the alkenyl group in the polymer (I); therefore,
20 care should be taken.

[0076]

The amount of the polymer (I) is not particularly restricted but is preferably such that the number of growing termini in atom transfer radical polymerization be equal to the
25 number of initiator groups in atom transfer radical polymerization in the polymer (I) to which said growing termini are to add. When the polymer (I) is used as an initiator for atom transfer radical polymerization from the beginning, numbers of an alkenyl terminus to be added and growing termini
30 are in principle equal, as already mentioned hereinabove. When another initiator is used, however, the number of growing termini becomes greater by the number of molecules of said initiator. It is therefore desirable to adjust the proportion thereof according to the desired multiblock copolymer.

35 [0077]

The polymer (I) may be added as such or in the form of a solution in a solvent which will not adversely affect the atom transfer radical polymerization.

<<Product

5 The multiblock polymer of the present invention is capable of combining various polymer block species, therefore it is possible to exhibit various physical properties such as oil, elastomer and plastics.

[0078]

10 In particular, it is preferred, though not requisite, a multiblock copolymer in which the polymer (I) have a glass transition temperature of not lower than 25°C and the polymer chain newly produced by atom transfer radical polymerization with the addition of the polymer (I) have a glass transition
15 temperature of not higher than 25°C or that the polymer (I) have a glass transition temperature of not higher than 25°C and the polymer chain produced by atom transfer radical polymerization upon addition of the polymer (I) have a glass transition
20 temperature of not lower than 25°C. Such multiblock copolymer is useful as a thermoplastic elastomer or an impact resistance improving agent described in the following.

<<Uses

<<Thermoplastic elastomer

25 The multiblock copolymer obtained by the production method of the present invention can be used in substantially the same fields of application as the existing styrenic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block copolymer with resins (with a plasticizer, a filler, a
30 stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and exterior, electric and
35 electronic fields, food wrapping films and tubes, drug

containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the multiblock copolymer obtained by the production method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, compatibilizing agent, flatting agent, heat resistance modifier or the like. Furthermore, when an isobutylene polymer block is contained, improvement of gas barrier property based on an isobutylene polymer can be expected.

[0079]

The thermoplastic resins which can be improved in shock resistance by addition of the multiblock copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and the like. Said multiblock copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and polyester resins, among others, are preferred since they can

readily show its characteristics such as improved weathering resistance and impact resistance.

[0080]

As the method of adding the multiblock copolymer of the present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0081]

Furthermore, in the resulting resin compositions, there may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether, and antimony trioxide; pigments such as titanium oxide, zinc sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0082]

[Effect of the Invention]

By adding, according to the present invention, polymers containing an alkenyl group at one terminus and a group serving as an initiator for atom transfer radical polymerization at the other terminus to a polymerization system for atom transfer radical polymerization, it is possible to obtain, with ease,

multiblock copolymers resulting from binding of various
polymers to one another. Furthermore, by producing the polymer
to be added by controlled radical polymerization, multiblock
copolymers well controlled in the molecular weight of the
5 polymer block to be bound can be obtained.

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its object to provide a multiblock copolymer composed of any of various polymers and a vinyl polymer produced by an easy production method without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] A multiblock copolymer which is produced by adding a polymer (I) containing an alkenyl group at one terminus and a group serving as an initiator group for atom transfer radical polymerization at the other terminus to an atom transfer radical polymerization system.

[Selective Figure] none